

STRUCTURE AND ION PAIRING INTERACTIONS IN PEO-LiX POLYMER ELECTROLYTES

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Although ionic conductivity in poly(ethylene oxide) (PEO) electrolytes has been shown to predominate in the amorphous phase [1], the structures of amorphous ether-LiX solvates are still largely unknown. These solvate structures are likely to be critical in determining the types of ionic conductivity mechanisms in PEO solid electrolytes. One approach to studying such solvation is to determine the crystal structures of $\text{PEO}_n\text{-LiX}$ complexes [2, 3] which represent the low energy, equilibrium structures formed for a given salt and concentration.

We have systematically studied the structures formed between ethers (glymes and PEO) with a wide variety of lithium salts. An explanation for the various crystal structures formed with the salts is given based upon the strength of ion-pairing interactions. These structures can be thought of in terms of solvent-separated ion pairs, contact ion pairs, and higher aggregates (Fig. 1). A scale of the strength of ion pairing in ether solvents is obtained through a comparison of the phases formed between glymes of increasing length and lithium salts with varying anions.

Phase diagrams of LiCF_3SO_3 with THF, monoglyme(G1), diglyme(G2), and triglyme(G3) are consistent with vibrational spectroscopy studies of ion pairing in these systems [4] and provide an explanation for the large fraction of 'free' anions observed in G2- LiCF_3SO_3 mixtures at low temperatures [5, 6]. This provides some insight into the structures of the amorphous liquid phases with low molecular weight ethers. Further, this should extend to high molecular weight PEO analogues as well to reveal how and why various structures form. Similar comparisons between phase diagrams, structural information, and vibrational spectroscopy studies in ether mixtures with salts such as LiSCN , LiNO_3 , LiCF_3CO_2 , LiClO_4 , LiBF_4 , LiPF_6 , LiAsF_6 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, and $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ which display a wide variety of ion pairing strengths should help clarify the localized structures in these systems at varying concentrations and temperatures.

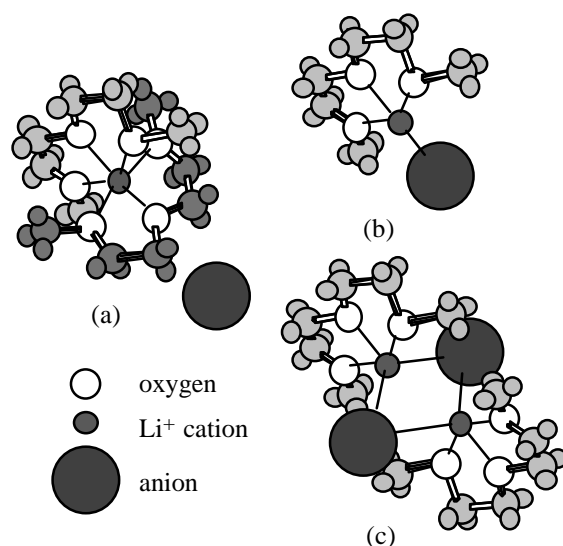


Figure 1. Schematic illustrations of possible diglyme-LiX (a) (2/1) solvent-separated ion pair, (b) (1/1) contact ion pair, and (c) (1/1) aggregate structures.

References

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